REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 1996	Professional Paper

4. TITLE AND SUBTITLE

STRAIN CHARACTERIZATION OF AsH_3 INDUCED EXCHANGE REACTIONS IN InP GROWN BY OMVPE

5. FUNDING NUMBERS

PR: EEB3
PE: 0602234N
WU: DN313033

6. AUTHOR(S)

A. R. Clawson and C. M. Hanson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Command, Control and Ocean Surveillance Center (NCCOSC)
RDT&E Division
San Diego, CA 92152–5001

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217–5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Behavior of As-P intermixing in heterojunctions of As-compounds grown on InP (001) has been inferred from strain of very thin mismatched layers inserted periodically in InP to form multilayer superlattice structures. Strain components are observed for both As-P exchange in the InP and from inserted layer growth. The data suggest that for As-compounds grown on an InP surface the availability of As for both layer growth and As-P exchange is rate-limited, most likely by surface kinetics, and an optimum growth rate occurs for minimizing the As-P exchange. There is also a fixed InAs strain component inherent to interfaces of As-compounds on InP. Monolayer thickness layers of AlP or GaP grown on the InP to change the surface chemical bonds are shown to reduce the As-P exchange somewhat but they do not stabilize the InP surface against exposure to AsH_3. H_2 and PH_3-exposures of the As-terminated surface show that P-As exchange to desorb the As is slow compared to As adsorption on InP by AsH_3 exposure.

19960523 212

14. SUBJECT TERMS

Mission Area: Microelectronics
Superlattice Structures
InP(001)
AsH_3

Strained Layers
Unstrained Binary Compound

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAME AS REPORT

DTIC QUALITY INSPECTED 1

UNCLASSIFIED

21a. NAME OF RESPONSIBLE INDIVIDUAL	21b. TELEPHONE *(include Area Code)*	21c. OFFICE SYMBOL
C. M. Hanson	(619) 553–5242	Code 8505

21a. NAME OF RESPONSIBLE INDIVIDUAL	21b. TELEPHONE *(include Area Code)*	21c. OFFICE SYMBOL

UNCLASSIFIED

Strain Characterization of AsH3 Induced Exchange Reactions in InP Grown by OMVPE

A. R. Clawson [†] and C. M. Hanson [§],

† Univ. California San Diego, ECE Dept-0407, 9500 Gilman Dr., La Jolla, CA 92093-0407
§ NCCOSC RDTE Div 555, 49285 Bennett St., Rm 111, San Diego, CA 92152-5790

Abstract. Behavior of As-P intermixing in heterojunctions of As-compounds grown on InP (001) has been inferred from strain of very thin mismatched layers inserted periodically in InP to form multilayer superlattice structures. Strain components are observed for both As-P exchange in the InP and from inserted layer growth. The data suggest that for As-compounds grown on an InP surface the availability of As for both layer growth and As-P exchange is rate-limited, most likely by surface kinetics, and an optimum growth rate occurs for minimizing the As-P exchange. There is also a fixed InAs strain component inherent to interfaces of As-compounds on InP. Monolayer thickness layers of AlP or GaP grown on the InP to change the surface chemical bonds are shown to reduce the As-P exchange somewhat but they do not stabilize the InP surface against exposure to AsH3. H2 and PH3-exposures of the As-terminated surface show that P-As exchange to desorb the As is slow compared to As adsorption on InP by AsH3 exposure.

1. Introduction

Compositional intermixing at InGaAs/InP heterojunctions has long been recognized as a limitation to achieving perfectly abrupt interfaces desired for device structures. It is generally concluded that intermixing on the group III sublattice is either small or negligible, but intermixing on the group V sublattice is significant[1,2]. Furthermore, the As-P exchange is different for the two different InGaAs/InP interfaces with resulting differences in heterojunction characteristics.

In this investigation we provide insight into the As-P intermixing behavior of As-compounds grown on InP substrates by analyzing the strain in periodic multilayer structures specially configured to reveal As-P exchange. The structures consist primarily of InP with very thin mismatched binary compounds inserted at ~170 Å spacing. A nominal "superlattice" of 30 periods is grown and analyzed by x-ray diffraction (XRD) to obtain a characteristic superlattice pattern. The separation of the superlattice zero order peak from the substrate (004) peak shows the change of average lattice dimensions due to elastic accommodation of different size atoms within the thickness of a 170 Å thick single period.

2. Experimental

The OMVPE growth was performed in a small scale horizontal reactor with a radiantly heated graphite susceptor at temperature of 650°C and pressure of 20 Torr on InP {001} substrates. Transient-free gas switching was achieved with a Thomas Swann Epifold low dead-space manifold using vent/run switching of established gas flows, keeping the gas flow to the chamber constant, and balancing the pressure between vent and run manifolds. Growth conditions to achieve reproducible growth rates were determined from previous studies[3,4].

Table 1 III-V OMVPE Growth Rates for This Study

III-V	⊥ Growth Rate (Å/second)	Measurement Technique
InP	2.24	from InP superlattice satellite peak spacing.
InAs	2.03	from InAs monolayer strain in GaAs superlattice.
GaAs	2.18	from GaAs superlattice satellite peak spacing.
GaP	2.52	from GaP monolayer strain in InP superlattice.
AlAs	2.34	from AlP = 2.19 Å/S assuming same Al atom per second rate.
AlP	2.19	from AlP monolayer strain in InP superlattice.

To analyze the strain it is important to accurately know growth rates to determine layer thicknesses. We have previously shown that fractional monolayer growth rates are the same as rates for thick layers, and that the strains of superlattices generally are predictable from the inserted layer thickness and mismatch[5]. Correction for the strain expansion or contraction of the layer's perpendicular lattice dimension is based on the Poisson ratio as outlined by Hornstra and Bartels[6]. We use the growth rates of these earlier studies as summarized in Table 1 to grow layers of predetermined thickness and strain. The measured superlattice strain is related to the individual strain components over the thickness of one period as:

$$(\Delta a_\perp/a)_{SL} \times d_{SL} = (\Delta a_\perp/a)_{ML} \times d_{ML} + (\ unknown \ ) \qquad (1)$$

$$i. \ e., [\text{superlattice strain}] = [\text{inserted layer strain}] + [\text{As-P intermixing strain}]$$

where $(\Delta a_\perp/a)_{SL}$ is the XRD measured superlattice strain, $d_{SL} = 170$ Å is the measured period thickness, $(\Delta a_\perp/a)_{ML}$ is the perpendicular strain of the elastically deformed thin "monolayer" calculated from its lattice parameter and elastic coefficients, and d_{ML} is the inserted monolayer thickness. The unknowns are the strain and thickness of the As replacement of P, which is easiest to describe as an equivalent thickness of InAs. Other possible strain components are considered insignificant. In particular, strains from group III sublattice intermixing contribute nothing to the superlattice strain[5], and data are presented below that show the rate of P replacement of As is comparatively slow thus we ignore its contribution. The superlattice strains resulting from thin As-compound layers inserted in InP are shown in Fig. 1. Three sets of data are shown: InAs layer growth, GaAs layer growth and InAs(P) formed by
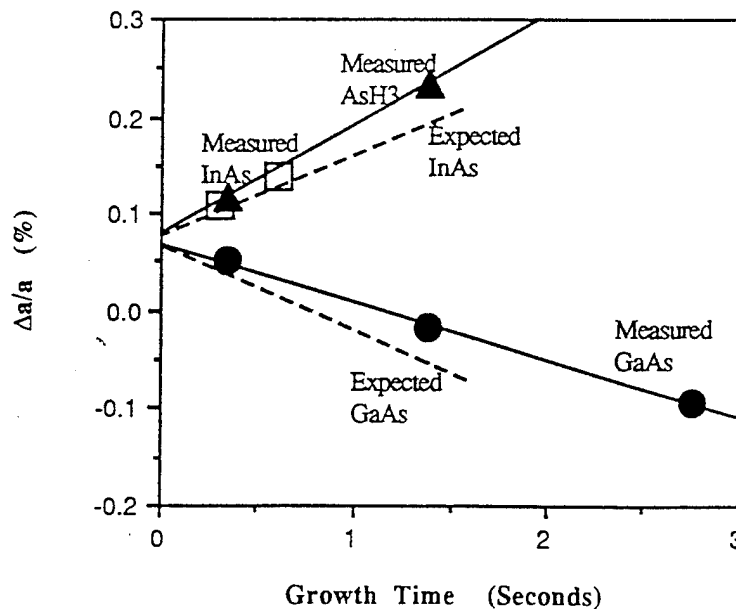

Figure 1. Strain in 30-period InP superlattices formed by periodic insertion of monolayer equivalent thicknesses of InAs (open squares) or GaAs (closed circles), or from AsH₃ exposure of InP (closed triangles) at 170 Å intervals.

periodic exposure of InP to AsH_3. The strains for each of the three kinds of layers increased with growth time, however, in each case the extrapolation to zero time shows an offset compressive strain component, $\sigma_0 \equiv \frac{\Delta a_\perp}{a}(t=0)$, equivalent to ~0.6 to 0.7 monolayers of InAs. σ_0 is a very rapidly formed strain attributed to a combination of In-As bonds formed when As preferentially replaces P on surface sites when InP is exposed to AsH_3 and As surface atoms that are relatively unaffected by subsequent exposure to PH_3.

An important feature of the data is evident by comparing the slopes of the measured strains of InAs and GaAs layer growth (solid lines) with their expected slopes (dashed lines). The difference between measured and expected slopes shows an additional time dependent compressive strain component, $\sigma(t) \equiv \frac{\Delta a_\perp}{a}(meas) - \frac{\Delta a_\perp}{a}(expected)$, which can only be attributed to formation of an As rich compound, InAs in our simplified view. It is significant that the rate of excess As-compound formation and therefore the quantity of As-compound causing the total strains for InAs and GaAs growths is the same and is also identical to the amount of InAs formed by exposure to only AsH_3. The implication is that the amount of available As to supply these growths is rate-limited to the same fixed amount, and that there are two mechanisms consuming the As: the layer growth preferentially uses whatever As necessary to achieve compound stoichiometry and the balance of As contributes to As-P exchange. In the absence of growth all the available As contributes to As-P exchange.

The As rate-limiting reaction step is attributed to the surface chemistry kinetics rather than to gas phase reactions. In Fig. 2 the strain is compared for AsH_3-exposed InP superlattices that are identical except for a 1.9 times increase in the concentration of AsH_3 used. The resultant strain dependencies on time are identical, thus the amount of As available to incorporation on the surface is unchanged; excess AsH_3 vapor has no effect. Only the σ_0 component has increased slightly.

There are several predictions for As-P exchange which can be made from this As rate-limited interpretation of the data in Fig. 1. One is that As-P exchange would be minimized if all the As is consumed in the layer growth. Another is that if a growth rate is established which exceeds the As available to maintain stoichiometry, it would result in a Group III rich surface which might result in liquid formation with consequent roughening and possible
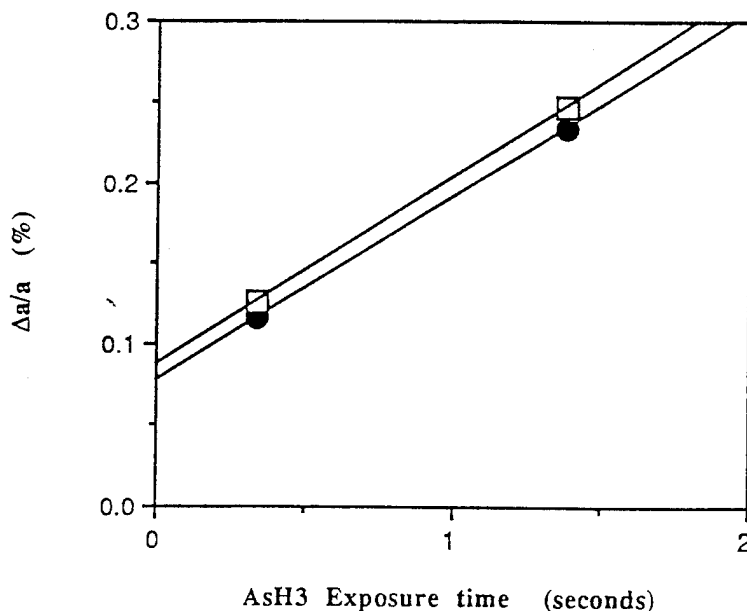

Figure 2. Strain of InAsP formed from AsH_3 exposure of InP at 170 Å intervals for 30 periods comparing effects of AsH_3 vapor concentration. Closed circles are for 0.008 mole fraction AsH_3 and open squares are for 0.0152 mole fraction AsH_3.

compositional intermixing when InP growth is resumed. There looks to be an optimum growth rate for As-compounds grown on InP.

To further explore the initial exposure of InP to AsH_3 the InP surface was capped with monolayers of AlP or GaP to change the surface atom bond strength as a means of stabilizing the InP surface against As-P exchange, as has been reported for OMMBE growth of InAlAs on InP[7]. Results shown in Fig. 3 compare strains of identical AsH_3 exposed superlattices with and without a cap layer of AlP or GaP. The strains of AlP-only and GaP-only in InP superlattices were determined for the zero AsH_3 exposure time, then structures with identical AlP or GaP monolayers were grown with additional AsH_3 exposure. The tensile strains from the AlP and GaP of -0.240% and -0.271% respectively, are fixed contributions to the total strain. The data of the strains with AsH_3 exposure extrapolate to a σ_0 that is identical to the offset without the cap layer. The absence of any change in σ_0 in the presence of AlP or GaP suggests that the interface displacement of surface P by As is the same. AlP or GaP monolayers were also grown following the AsH_3 exposure and again no change is seen in σ_0. On the other hand, $\sigma(t)$ is sensitive to AlP and GaP cap layers on the InP surface, and for both shows a decrease in the compressive strain when the cap layers are grown prior to AsH_3 exposure, while there is little or no effect when the cap layer are grown after the AsH_3 exposure.

To further assess the behavior of the As-terminated surface the desorption of As during exposure to H_2-only or H_2+PH_3 atmospheres was studied. Fig. 4 shows the results of a 1.38 second AsH_3 exposure of InP followed by an exposure of the As-terminated surface to varying periods of H_2 or PH_3 prior to resuming InP growth of the superlattice. The only strain which could be introduced in these structures would be compressive, from InAs. Exposure to H_2 shows negligible desorption of As. This relates to the apparent InGaAs surface stability that allows use of H_2 interrupts at this interface to improve interface abruptness[8,9]. The interrupt allows time to fully deplete the very reactive arsine vapor with no degradation of the surface prior to starting InP growth. The decrease of strain when the As-terminated surface is exposed to PH_3 indicates removal of As and its replacement by P. The rate of P-As exchange of the As-terminated surface in the presence of phosphine is at a much slower rate than the rate of As-P exchange in the presence of arsine. There is a distinct change in the rate of As desorption when the strain is reduced to the equivalence of ~2/3
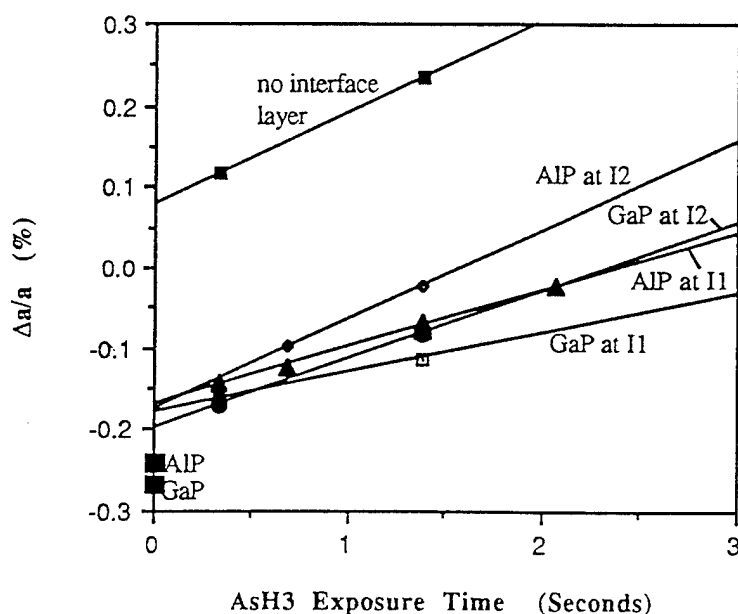

Figure 3 Strain of InAsP formed from AsH_3 exposure of InP at 170 Å intervals for 30 periods showing effects of adding an interface layer on the InP of ~1 monolayer AlP or ~1 monolayer GaP prior to AsH_3 exposure (interface I_1) or following the AsH_3 exposure (interface I_2).
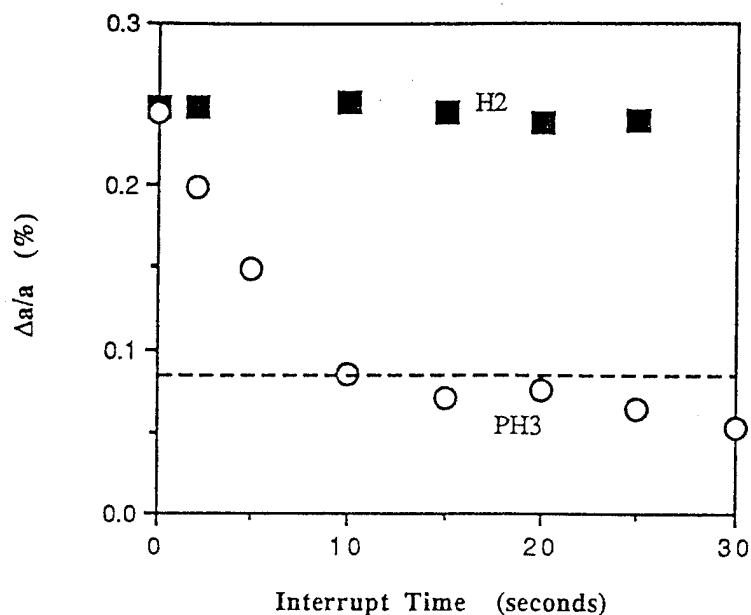
Figure 4. Strain in InP 30 period superlattices formed by periodic insertion of 1.38 second AsH$_3$ exposure followed by an As-desorption growth interrupt in H$_2$ or H$_2$+PH$_3$ at 170 Å intervals. The dotted line is the expected strain for inclusion of the ~2/3 monolayer InAs in the superlattice equivalent to σ_0 from figure 1.

monolayer InAs suggesting that the As is more easily removed when in excess of 2/3 monolayer of InAs.

Using the data of Fig. 4 along with Fig. 1, both σ_0 and $\sigma(t)$ might be interpreted in terms of surface reconstruction. For As-compounds formed on InP from AsH$_3$ the occurrence of σ_0 equivalent to ~2/3 monolayer InAs seems to be a fundamental feature. This suggests that a stable surface on InP exposed to AsH$_3$ has a single layer surface reconstruction with only partial occupancy of the surface sites. The offset strain, σ_0, is envisioned as forming partly when As substitutes for P on the surface at the start of As-compound growth and partly when the InP growth resumes on the As-terminated surface. The time-dependent strain, $\sigma(t)$, is envisioned as resulting from a multilayer accumulation of adsorbed As in excess of the semiconductor surface layer analogous to the multiple dimer layers seen for c(4x4)/d(4x4) GaAs surface reconstruction. This excess could then release into the next InP layer as the surface adjusts to the observed equilibrium InP single layer (2x4) reconstruction[10].

3. Conclusions

Superlattices formed by periodic insertion of strained layers into an unstrained binary compound can be used to elucidate characteristics of group V exchange across heterojunction interfaces. Excess compressive strain when As-compounds are grown on InP is attributed to As replacement of P, and the excess InAs strain component can be separated from the expected strain of the inserted thin layer. Strains of thin As-compound layers grown in InP show that during growth the amount of As available for reaction either in layer growth or in As-P exchange is rate-limited by surface kinetics, and an optimum growth rate should provide stoichiometric layer growth with minimum As-P exchange. Modification of the InP surface chemical bond strength by growing monolayers of AlP or GaP has some effect on reducing As-P exchange but does not stabilize the InP surface against AsH$_3$ exposure for the OMVPE growth conditions. For As-terminated surfaces exposed to PH$_3$ the P replacement of As is a slow reaction compared to As replacement of P under AsH$_3$ exposure. Indication of a stable ~2/3 coverage As surface layer on InP suggests that a part monolayer of InAs at each interface

is inherent to growth of As-compounds in InP, and additional excess As from accumulation on the As-compound surface can carryover into subsequent InP growth.

Acknowledgements

References

[1]. J. P. Wittgreffe, M. J. Yates, S. D. Perrin and P. C. Spurdens, *J. Crystal Growth* 130, 51-58 (1993)

[2]. R. Meyer, M. Hollfelder, H Hardtdegen, B. Lengeler and H. Lüth, *J. Crystal Growth* 124, 583-588 (1992)

[3]. A. R. Clawson, T. T. Vu, S. A. Pappert and C. M. Hanson, *J. Crystal Growth* 124, 536-540 (1992)

[4]. A. R. Clawson, X. Jiang, P. K. L. Yu, C. M. Hanson and T. T. Vu, *J. Electron. Mater.* 22, 423 (1993)

[5]. A. R. Clawson and C. M. Hanson, presented at the Electronic Materials Conference, June 22-24, 1994, Boulder, CO; submitted to *J. Electron. Mater.*

[6]. J. Hornstra and W. J. Bartels, *J. Crystal Growth* 44, 513-519 (1978)

[7]. W. E. Quinn, M. C. Tamargo, M. J. S. P. Brazil, R. E. Nahory and H. H. Farrell, *J. Vac. Sci. Technol.* B 10, 978-981 (1992)

[8]. N. J. Long, A. G. Norman, A. K. Petford-Long, B. R. Butler, C. G. Cureton, G. R. Booker and E. J. Thrush, *Microsc. Semicond. Mater. Conf.*, Oxford, 25-28 March 1991 (Inst. Phys. Conf. Ser. No. 117; section 2) p. 69-74

[9]. A. Kohl, A. Mesquida Küsters, S. Brittner, K. Heime, J. Finders., D. Gnoth, J. Geurts and J. Woitok, *Proc. 6th Int'l. Conf. on Indium Phosphide and Related Materials*, March 27-31, 1994, Santa Barbara, CA (IEEE Cat.No. 94CH3369-6) p. 151-154

[10]. J. Jönsson, F. Reinhardt, K. Ploska, M. Zorn, W. Richter and J.-Th. Zettler, *Proc. 6th Int'l. Conf. on Indium Phosphide and Related Materials*, March 27-31, 1994, Santa Barbara, CA (IEEE Cat.No. 94CH3369-6)p.53-56